

Durability of Concrete in Marine Environment--A Review

By P. Kumar Mehta

Synopsis: Case histories of deteriorated portland-cement concretes exposed to sea water, both in mild and cold climates, show that permeability is the most important characteristic determining the durability of concrete. Whether due to improper mix proportions, or poor concreting practice, or cracking of concrete, permeable concretes tend to deteriorate in marine environment. This is because the hydration products of portland cement are chemically unstable to certain aggressive components present in sea water.

In this paper, the chemical reactions between the aggressive components of sea water and the constituents of hydrated portland cement are reviewed. The physical processes of deterioration associated with these chemical reactions are discussed. Also discussed are the fundamental anodic and cathodic reactions involving corrosion of reinforcing steel in concrete exposed to sea water. A summary of recent work on the effectiveness of various admixtures in reducing the permeability of hydrated portland cement is given.

Keywords: admixtures; cathodic protection; climate; concrete durability; corrosion; cracking (fracturing); deterioration; harbor structures; hydration; marine atmospheres; mix proportioning; permeability; portland cements; reinforcing steels; sea water.

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INTRODUCTION

Oceans make up 80 percent of the surface of the earth. This means that the area covered by the oceans is four times larger than the area covered by land. Mans' earliest uses of ocean were for navigation and fishing, however pressures of the growing world population and a corresponding demand for resources is rapidly extending the sphere of a wide variety of human activities to the continental shelves. Already, a fifth of our oil and gas comes from the off-shore facilities. Seabed mining for mineral resources is a distinct possibility in the near future. Manganese nodules present in large quantities in the North and South Pacific can become a major source for supplies of metallic manganese, nickel, copper, and cobalt. In order to relieve the land from pressures of urban congestion and pollution, consideration is being given to the idea of locating cities, airports, nuclear power and waste disposal plants on offshore floating platforms.

Piers, foundations, retaining walls and breakwaters for sea structures are generally made of portland cement concrete. Production and storage facilities on seabeds for exploitation of energy and mineral resources would be made of concrete. Also, if the oil storage tanks in the North Sea are indicative of the trend, most sea structures of the future would continue to be made from portland cement concrete. This is because in the context of the aggressive nature of sea water, concrete is not only the most economic structural material for construction of large structures, but also is the most durable, requiring little or no maintenance during the service life of the structure. Furthermore, in this period of energy consciousness, concrete is expected to replace other structural materials which require much more energy to produce. For instance, for a given load, a prestressed or reinforced concrete member can be made at the expense of 1/4th to 1/6th as much energy as the corresponding steel member.

However, this trend toward more and larger concrete structures, exposed to deeper and rougher sea waters, places an unusual demand on the safety and long-term reliability of structures. Consequently, a fresh look at the subject of durability of concrete in marine environments is needed. Whereas well-made structures of high quality concrete have lasted hundreds of years in sea water, others of inferior workmanship or poor quality concrete are known to have deteriorated. In this paper, case histories of

deteriorated concrete exposed to sea water are reviewed in order to arrive at a basic understanding of the various ways in which concrete can deteriorate. The physical processes of concrete deterioration are identified, and the associated chemical reactions between the components of sea water and the constituents of hydrated portland cement are discussed in detail. Also discussed are the anodic and cathodic reactions responsible for corrosion of reinforcing steel in concrete exposed to high concentration of chloride ions present in sea water. In the end, since the permeability of concrete is the most important factor determining long-term durability of concrete sea structures, and since permeability of concrete is greatly influenced by the permeability of cement paste, a brief summary of recent work at the University of California is given on the effect of several admixtures on reducing the permeability of hydrated portland cement.

CASE HISTORIES OF CONCRETE DETERIORATION IN MARINE ENVIRONMENT

In 1924, Atwood and Johnson (1) published their comprehensive review of the state-of-the-art on the previous 100 years of experience with concrete in sea water. The oldest cementing material cited in the paper consisted of a 60 A.D. lime-pozzolan mortar which, when compared with five recent (1886-1899) mortars, showed that after removal of a part of the original lime present by sea water, the residual lime content in all the six specimens was similar. According to Feld (2), recognition of possible concrete deterioration due to chemical alteration by sea water exposure came as early as 1880, when Professor Prazier of the University of Aberdeen, Scotland, investigated the causes of deterioration of concrete at Aberdeen Harbor. He warned that hydraulic cements used in concrete exposed to sea water would absorb magnesia by ion exchange, resulting in loss of lime and surface disintegration. Further, according to Feld, M. Vicat in France, in his study of disintegration of lime-pozzolan concrete blocks at Marseilles, Rochefort, Algiers, and Cherbourg, arrived at the same conclusions.

From the standpoint of some of the earliest published data on deterioration of portland-cement concrete in sea water, the following three reports cited by Atwood and Johnson (1) are of considerable interest:

(i) A 1920 report by the British Institute of Civil Engineers to the International Navigation Congress on 30 concrete structures, six constructed during 1855-1880 and the remaining 24 during 1880-1912, showed that 17 of the thirty structures were in a state of deterioration. Among the 13 which showed no deterioration, one had a granite facing and four contained pozzolan as admixture in concrete.

(ii) A report of portland cement concrete damage from Port-of-Spain showed that a breakwater was built with 90-day cured concrete which was fully submerged 12 meters below the low-tide line. Within five years, the concrete was found in a state of deterioration. Chemical analysis of cement paste showed con-

siderable loss of lime, and large increases in MgO and CO_2 content.

It can be concluded that fully submerged portland-cement concrete is vulnerable to chemical decomposition by the magnesium salts and CO_2 present in sea water.

(iii) A 1922 report of the San Francisco Bay Marine Piling Committee showed that 457 reinforced concrete cylinders needed repairs from a total of 5198 installed during 1909-1918. In two badly damaged structures, over 25 percent piles showed cracks over the reinforcement above the high-tide line, within ten years of installation.

From this it was concluded that in the case of reinforced concrete, a direct contact between the structure and sea water is not essential for corrosion of steel in concrete and the associated phenomenon of concrete cracking.

Further review of case histories of concrete deterioration in sea water shows that it is desirable to study separately the performance of sea structures in mild climates and cold climates, because in the latter case the effect of freeze-thaw cycles on concrete is often superimposed on the effect of sea water. Tables 1 and 2 contain a summary of some reports on performance of concrete sea structures in mild climates and cold climates, respectively.

CONCRETE EXPOSED TO SEA WATER IN MILD CLIMATES

Regourd (3) studied the effect of 66 years exposure of portland-cement mortars made with different cement contents, 300, 450, and 600 kg/m^3 . Lean mortars were severely damaged, however the dense cubes containing 600 kg/m^3 cement, even when made with a 14.9% C_3A cement, remained in good condition. The chemical resistance of cements was found to be significant only in the case of mortars with low cement content which were, therefore, more permeable. In general, portland pozzolan and slag cements which contain less free lime on hydration than pure portland cement, showed better resistance to sea water. Also, irrespective of the type of cement originally used, the deteriorated samples contained the same constituents, namely, calcium carbonate in the form of calcite or aragonite, brucite, and magnesium silicate hydrate. In later work on highly carbonated mortars from the offshore dike in the Cherbourg Port, Regourd et al (4) identified the presence of gypsum, ettringite, and a carbonated form of ettringite, called thaumasite.

Mehta and Haynes (5) reported the results of their investigation on 67 years old unreinforced concrete blocks, made with six different portland cements and three different concrete mixtures, which remained in partially submerged condition in sea water in the Los Angeles harbor. Dense concrete blocks, some made with a 14-15% C_3A portland cement, were still in excellent condi-

tion, however, lean concrete showed loss of material and was soft and weak. The cementing constituents originally present, namely CSH and CH, could not be detected in the samples of deteriorated concrete which showed considerable amounts of brucite and gypsum, and small amounts of aragonite, ettringite, and hydrocalumite (carboaluminate hydrate) present. Thus, this investigation confirmed that permeable portland cement paste is inherently unstable to magnesium salts, sulfate ions, and CO_2 present in sea water.

Results of investigations on over 40 years old reinforced concrete structures exposed to sea water on the west coast of the United States are given by Wakeman et al (6), and a subsequent discussion of this paper by Fluss and Gorman (7). In the Los Angeles harbor, precast reinforced concrete piles were driven in 1912 to support a 800-meters wharf. After 12 years of service, some piles showed longitudinal cracks at the mid-tide level, leading eventually to crumbling and spalling of concrete. The concrete below the low-tide line remained sound. It was postulated by Wakeman et al (6) that corrosion of the reinforcements in concrete by permeation of sea water through fissures probably caused by sulfate attack were responsible for the problem. In 1958, Fluss and Gorman (7) reported on the reinforced concrete cylindrical piles and girders of the San Francisco ferry building constructed in 1912. Good quality concrete containing 658 lbs/yd³ (395 kg/m³) of Type I portland cement was used. After 46 years of service, most of the piles were found in good condition in spite of the high (14-17%) C_3A content of the cement. However, one-fourth of the cast-in-place piles and one-third of the transverse girders for Pier Nos. 26 and 28 were found cracked. It was speculated that the presence of micro-cracks in concrete due to excessive deflection under load might have exposed the reinforcing steel to the corrosive action of sea water. Also, poor workmanship was held responsible for differences in permeability of in-place concrete, although the concrete mixture was of satisfactory quality.

Several examples of damage to concrete sea structures are given by Feld (2). After 21 years of use, the concrete piles and caps of the trestle bents of the James River Bridge at Newport News, Virginia, required a \$1.4 million repair and replacement job in 1955, when 70 percent of the 2500 concrete piles were found in need of repair. Some 750 precast concrete piles driven in 1932 near Ocean City, New Jersey, had to be repaired in 1957 after 25 years of service. The severity of the loss of material from the piles, caused by higher than normal concentrations of dissolved CO_2 in sea water, can be judged from the fact that the 550 mm dimension of some piles had been reduced to 300 mm. The bridge over the Shrewberry River, New Jersey, built in 1913, had 10 piers, two of which showed signs of failure about a year after they were built. Concrete had been placed by tremie, and alternate layers of concrete and a soft putty containing salt crystals was found on the removal of these piers. Laitance accumulation of 50 to 75 mm in 5 meter depth of concrete placement was common when placing concrete using gravel as aggregate. However, with crushed stone as aggregate, the laitance layer was twice as thick.

Complete removal of such laitance layers should have been done to avoid permeable seams which are first to be subjected to sea water action.

CONCRETE EXPOSED TO SEA WATER IN COLD CLIMATES

Table 2 shows a summary of the results of surveys by Idorn (8), and Gjorv (9) on the performance of mostly 20-50 years old coastal concrete structures in Denmark and Norway, respectively. Pier No. 7 of the Oddesund Bridge in Jutland, Denmark, had to be repaired after 8 years of service. Examination of deteriorated concrete indicated decomposition of the cement and loss of strength below low-tide level, and cracking due to freezing and thawing above high-tide level. Aragonite, ettringite, gypsum, brucite, and alkali-silica gel were detected as the products of cement decomposition. History of structure indicated that caissons were initially cracked due to thermal stresses in concrete, and this could have permitted percolation of sea water into the interior of concrete. The piers of a highway bridge in North Jutland showed severe cracking and spalling at the mean-tide level, producing the typical hour-glass shape, which is characteristic of concrete cylindrical piles exposed for long time to sea water. The failure was caused by poor quality (high water-cement ratio) concrete which was vulnerable to degradation through severe corrosion of reinforcement, freezing and thawing, and alkali-aggregate reaction. Concrete blocks from Groin 71 at the north barrier of the Lim Fiord, Denmark, were found severely deteriorated in 20 years of exposure to sea water. The concrete was very weak as a result of decomposition of the cementitious component. Poor quality of concrete mixture, which contained only 370 lbs/yd³ (220 kg/m³) cement, exposure to repeated cycles of wetting - drying, freezing - thawing, and impact of gravel and sand present in the surf were considered responsible for the loss of material.

In 1962-64, Gjorv (9) surveyed 716 concrete structures along the Norwegian seaboard. At the time of the survey, about two-thirds of the structures were 20-50 years old. He found that, in general, concrete pillars were in good condition both above the high-tide line and below the low-tide line. In the tidal zone, about 50 percent of the surveyed pillars were in good condition while others showed signs of damage. Fourteen percent pillars had more than 30 percent reduction in area of cross section, and twenty-four percent had 10-30 percent reduction. This deterioration was ascribed mainly due to the effect of frost action for which the concrete was not designed. Among the numerous other examples of cracking and disintegration of reinforced concrete sea structures in cold climates is Pier No. 2 of a concrete wharf in Halifax, Nova Scotia, which according to Tibbetts (10) needed extensive repairs. The concrete in the tidal zone was protected with timber jackets but it cracked above the high-tide line, probably due to the combined effect of freeze-thaw cycles and corrosion of the reinforcement.

LESSONS FROM CASE HISTORIES OF DETERIORATED CONCRETES

The first lesson from the case histories of concrete damage in sea water is that portland-cement concretes invariably contain seeds of potential deterioration. These seeds are present in the form of the hydration products of portland cement, especially calcium hydroxide, which being basic in nature, are vulnerable to chemical decomposition as a result of chemical interaction with certain components of sea water, namely $MgCl_2$, $MgSO_4$, and CO_2 .

Whether these seeds turn into deleterious products depends mainly on the ability of a concrete to keep water from penetrating into the interior. Thus, the second lesson from the above case histories of concrete failures is that permeability of concrete is the most important property determining long-term durability. Again, from the case histories of deteriorated concretes, the following causes for lack of water-tightness can be identified:

(i) Improper mix design: Permeability of concrete is derived mainly from the permeability of cement paste. Low cement content and high water-cement ratio produce a readily permeable product on hydration. Poorly graded aggregate can also be a source of lack of water-tightness.

(ii) Poor Concreting Practice: Even a high quality concrete mixture can yield a permeable concrete if the concrete is not properly compacted. Poorly constructed joints can also permit percolation of water. Carelessness in placement, such as segregation of concrete mixture and formation of thick layers of laitance at joints, or dilution of concrete mixture with additional water, has frequently been identified as a source of concrete permeability.

(iii) Cracks in Concrete: Despite good quality of concrete and proper workmanship, concrete structures may yet be permeable to sea water if they develop cracks during the course of their service life. Among the common sources of cracking are excessive deflection due to load, carelessness in transporting precast members and driving precast piles, thermal stresses due to temperature gradient in thick concrete structures, freeze-thaw cycles on non-air-entrained concrete, corrosion of reinforcing steel and expansive chemical reactions such as these involving formation of ettringite and alkali-silica gel.

Another lesson from the case histories of concrete deterioration in sea water is that, depending on the tidal lines, the individual processes of deterioration tend to limit themselves to different parts of a structure. From this standpoint a structure can be divided into three zones which are illustrated by Fig. 1. The uppermost part, which is above the high-tide line, is not directly exposed to sea water. However, it is exposed to atmospheric air, winds carrying sea salts, and frost action. Con-

sequently, cracking due to corrosion of reinforcement in concrete and/or freezing and thawing of concrete are the predominant deleterious phenomena in this zone. The structure in the tidal zone, which is between high-tide and low-tide mark, is not only vulnerable to cracking and spalling of concrete due to wetting and drying, frost action, and corrosion of reinforcement, but also to loss of material due to chemical decomposition of hydration products of cement, and impact of waves containing floating ice, sand, and gravel. The lower part of the structure, which is always submerged in sea water is vulnerable to strength retrogression and loss of material as a result of the chemical reactions between sea water and hydration products of cement. Due to the absence of frost action and due to lack of oxygen, cracking of concrete due to freeze-thaw cycles and corrosion of the reinforcing steel is seldom a problem here.

CHEMISTRY OF REACTIONS BETWEEN SEA WATER AND HYDRATION PRODUCTS OF PORTLAND CEMENT

The chemistry of reactions responsible for the decomposing action of sea water on the constituents of hydrated portland cements is summarized in Table 3. Before a discussion on the subject, it is desirable to briefly review the relevant features of sea water composition, and microstructure of hydrated portland cement paste.

Typically, sea water contains about 3.5 percent soluble salts by weight. The relative ionic concentrations in grams per liter are 18 gpl Cl^- , 12 gpl Na^+ , 2.6 gpl $(\text{SO}_4)^{2-}$, 1.4 gpl Mg^{2+} , and 0.5 gpl Ca^{2+} . In terms of chemical salts, the composition of sea salt can be expressed as 2.7 gpl NaCl , 0.32 gpl MgCl_2 , 0.22 gpl MgSO_4 , and 0.13 gpl CaSO_4 . Whereas the presence of chloride ions in sea water has considerable influence on corrosion of steel in concrete, it is the magnesium salts present which exercise the most harmful effect on the hydration products of portland cement. Carbon dioxide dissolved in sea water can also become instrumental in decomposing a hardened cement paste. Normally, the pH of sea water is about 8 and only very small amounts of dissolved CO_2 are present. However at times, due to presence of decaying organic matter, highly carbonated sea waters show pH values of 7 or less, and they can be quite deleterious to the hydration products of portland cement.

Well-hydrated pastes of ASTM Type I/II portland cement consist mainly of a microcrystalline calcium silicate hydrate, having an approximate chemical composition, $3 \text{CaO} \cdot 2 \text{SiO}_2 \cdot 3 \text{H}_2\text{O}$, and two hydrates which are well crystalline, namely calcium hydroxide and the monosulfate hydrate, $3 \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 18\text{H}_2\text{O}$. The latter is responsible for the expansive reaction involving formation of ettringite when hardened pastes of Type I/II portland cement are exposed to sulfated water. The monosulfate is not present in the hydration products of Type V portland cement.

Completely hydrated pastes of pure portland cement contain

about 24 percent Ca(OH)_2 by weight, and this is the most vulnerable constituent of cement paste from the standpoint of ease of attack by the aggressive components of sea water, such as CO_2 , MgCl_2 , and MgSO_4 . As discussed in Table 3, some of the products of chemical interaction between Ca(OH)_2 and the aggressive components of sea water being soluble in sea water, lead to removal of Ca(OH)_2 from the hardened cement paste - a phenomenon associated with weakening of the material and loss in its strength. Increased permeability caused by lime leaching exposes the other constituents of cement paste to carbonation attack. Thus, eventually, even the principal cementitious phase, $3 \text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$, can be destroyed, as shown in Table 3.

Several investigators have shown that cements which contain little or no Ca(OH)_2 on hydration are more durable to chemical attack of the type discussed above. In a study involving 30 years of immersion in sea water of 2500 concrete specimens, made with 18 different kinds of cements and mixtures having 0.55 to 0.65 water-cement ratio, Gjorv (11) established that concretes made with calcium aluminate cement, supersulfated cement and blastfurnace slag cements resisted the action of sea water fairly well, even when the specimens were not cured prior to immersion in sea water. However, even the low C_3A portland cements were affected. Addition of trass, a pozzolan, greatly improved the durability of the cement.

As will be discussed later, in reinforced and prestressed concrete, some reserve basicity provided by the presence of free lime in hydrated cement paste is considered useful for protection of steel from corrosion. However, for protection of both steel and concrete from attack by sea water, it is desirable to remove a part of the potential free lime by pozzolan addition to concrete. Simple calculations show that addition of 15 percent of a good-quality pozzolan (by weight of cement) to a portland-cement concrete mixture will be able to remove only one-half of the potential free lime from well-hydrated cement paste. Similarly, in response to a discussion of her paper, Regourd (3) pointed out that portland cements containing belite as the principal silicate phase, rather than alite, will be more resistant to sea water because hydration of belite liberates less lime.

There is considerable confusion in published literature regarding the role of C_3A in portland cement on sulfate resistance of concrete exposed to sea water. Several investigators, including Regourd (3), Mehta and Haynes (5), and Fluss and Gorman (7) found excellent long-term durability of relatively rich (low water-cement ratio) concretes made with portland cements of 12-17 percent C_3A content. Although, ettringite in minor quantities was detected in deteriorated concrete, ettringite has seldom been conclusively demonstrated to be the sole cause of cracking of an off-shore concrete structure exposed to sea water. This is because the presence of chlorides, as in sea water, inhibits the expansive phenomenon associated with ettringite. Lea (12) states that, according to Batta, the reactions involving formation of ettringite and gypsum are not accompanied by swelling to the same degree in

sea water as in pure solutions of sodium or magnesium sulfate because both ettringite and gypsum are more soluble in solutions containing chlorides.

Attention has been drawn to the possibility that different crystalline forms of C_3A may show different degrees of resistance to sulfates in sea water. Regourd (3) studied the hydration characteristics of both synthetic and industrial cements containing cubic, orthorhombic or tetragonal C_3A . The pastes containing orthorhombic or tetragonal C_3A , made with 0.5 water-cement ratio and allowed to hydrate in sea water, showed at 90 days more chloroaluminate hydrate than ettringite. The reverse was observed when the C_3A phase in cement was in the cubic form. This implies that the presence of cubic C_3A , instead of orthorhombic or tetragonal C_3A , will make a portland cement more vulnerable to sulfate attack associated with ettringite. Recent unpublished work by this author did not confirm this.

Cole (13) identified the presence of a magnesium silicate hydrate, $4MgO \cdot SiO_2 \cdot 8H_2O$, in samples of old concrete subjected to prolonged sea water exposure. Regourd (3) observed that the presence of magnesium silicate hydrate made the specimens friable and weak. In Table 3, the chemical reaction is shown by which magnesium sulfate of sea water converts the principal cementing products in portland cements, namely the calcium silicate hydrate and lime, to the magnesium silicate hydrate and gypsum. In the synthetic cements of Regourd (3), it was reported that more magnesium silicate hydrate was formed when the cement contained tetragonal or orthorhombic C_3A rather than cubic C_3A .

POSSIBLE PATTERN OF CHEMICAL DECOMPOSITION OF CEMENT PASTE IN SEA WATER

Biczok (14) cites a possible pattern, proposed by Moskvina, on the progress of chemical reactions into the interior of a hardened portland-cement paste exposed to sea water. Concrete surface can be considered as the first zone of sea water attack. As a result of Ca^{++} and OH^- ions moving out to the concrete surface, aragonite is generally precipitated at the surface. In highly carbonized sea water, aragonite is converted to bicarbonate, and being soluble it is leached away. The action of CO_2 present in sea water is thus limited to the concrete surface. The second zone is the zone of Mg^{++} ion attack. Dense precipitates of $Mg(OH)_2$ (brucite) are generally found here, while SO_4^{--} and Cl^- ions continue to move further into the interior of the cement paste where, in the third zone, the chloroaluminate hydrate and sulfoaluminate hydrate (ettringite) are formed.

According to Kalousek and Benton (15), the Mg^{++} cannot penetrate into the paste so long as supply of OH^- to the paste surface-solution interface is maintained. When OH^- ion concentration is depleted at an advanced state of deterioration, Mg^{++} ion penetration into paste can occur, thus exposing the calcium silicate hydrate to Mg^{++} ion attack.

In the third zone, formation of gypsum and ettringite is responsible for removal of the SO_4^{--} ions from sea water. The Cl^- ions continue to penetrate deeper into the interior. Many investigators including Kalousek and Benton (15) found significant quantities of chloride penetration even into 0.3 water-cement ratio pastes. Obviously, this is due to the fact that except for the chloride, the components of sea water, such as CO_2 , Mg^{++} and SO_4^{--} , are readily removed in the outer zones as a result of the chemical reactions with cement paste.

Although C_3A and C_4AH_{19} , if present in a hydrated cement paste, are capable of removing chloride ions as chloroaluminate hydrate, this compound is not stable in a sulfate environment. Thus, on exposure to the sulfate ions present in sea water, the chloroaluminate converts to ettringite, releasing the chloride ions. Kalousek and Benton (15) submit this as a likely explanation for the increasing amounts of ettringite in the deep interior of the paste, with simultaneous presence of chloride. This explanation also accounts for the absence of the chloroaluminate in the outer zone of the paste, even when high- C_3A portland cements were subjected to prolonged exposures by sea water.

CORROSION OF STEEL IN CONCRETE

Corrosion of steel in concrete is an electrochemical process which depends mainly on electrical resistivity of the material, pH of the cement paste in contact with steel, and diffusion of chlorides and oxygen into the concrete. For moist concretes in offshore structures, the electrical resistivity is generally low and is, therefore, not a limiting factor for the corrosion to occur. The concentration of dissolved oxygen in sea water is usually less than 10 ml/l, however it is about 210 ml/l in air, thus providing far better conditions for corrosion in the atmospheric and tidal zones than in the submerged zone of a structure.

In the presence of chloride and hydroxyl ions, and oxygen, the anodic and the cathodic reactions can be represented as follows.

- (i) Anodic reaction, assuming high $(\text{OH})^-$ concentration:

$$\text{Fe} + 3(\text{OH})^- \rightarrow 1/2 \text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 3\text{e}^-$$

The hydrated iron-oxide, being insoluble in alkaline environment forms a protective film on steel, thus preventing any further loss of material.

- (ii) Anodic reaction assuming high Cl^- concentration:

$$\text{Fe} + 2 \text{Cl}^- \rightarrow \text{FeCl}_2 \rightarrow \text{Fe}^{++} + 2\text{Cl}^- + 2\text{e}^-$$

- (iii) Cathodic reaction, if oxygen is present:

$$1/2 \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2(\text{OH})^-$$

It is obvious from the above reactions that high concentrations of chloride and oxygen would favor the corrosion of

steel, whereas a high concentration of $(OH)^-$ would retard it. There is a threshold value of $Cl^-/(OH)^-$ for which the probability of formation of the protective hydrated iron-oxide film according to reaction (i) becomes equal to the probability of occurrence of the corrosive anodic reaction (ii). This threshold value, corresponding to 0.63, represents the minimum $Cl^-/(OH)^-$ ratio needed to initiate corrosion. Below this concentration, steel corrosion is not likely to occur. Thus, in the atmospheric zone and tidal zone of an offshore structure, the rate of corrosion of steel in concrete would depend mainly on the chloride concentration and the pH of the concrete which is in contact with the steel.

A possibility is suggested by some investigators that in high- C_3A portland cements, even a higher $Cl^-/(OH)^-$ ratio than 0.63 may be tolerated because of the ability of the C_3A to remove some chloride by the formation of the chloroaluminate, $C_3A \cdot CaCl_2 \cdot 11H_2O$. Mehta (16) showed that ASTM Type II and Type V portland cements do not contain enough C_3A available to provide for this type of protection to concrete in sea water, because up to 8 percent C_3A in cement is preferentially consumed by 5 percent gypsum, which is normally present in commercial cements. Verbeck (17) found that in 25 years, test piles of reinforced concrete made with high C_3A (8-11%) cements showed less cracking in sea water at St. Augustine, Florida, than similar piles made with low C_3A (2-5%) cements. Since, eventually, the chloroaluminate is not stable in sulfate waters, its formation in cements containing more than 8 percent C_3A , may provide only a temporary relief from the chloride corrosion phenomenon in sea water, if the concrete is permeable.

As already discussed, since chloride ions are not removed from sea water by chemical reactions with the constituents of hydrated portland cement paste, they are capable of deep penetration even in high-quality concrete. Therefore, in the final analysis, the pH of the cement paste becomes the controlling factor for the corrosion process. Depending on alkali content of a portland cement, the pH of hydrated cement paste is generally between 13 and 13.5. Significant corrosion rates in the presence of chloride are reported to occur only when the pH is reduced below 11.5. Gjorv and Vennesland (18) found that addition of as much as 20 percent sodium chloride, the major salt present in sea water, did not reduce the pH. Of the various ions present in sea salt, it is the magnesium ions which have the most pronounced effect on the pH because of their ability to remove the hydroxyl ions from the solution phase in the form of relatively insoluble $Mg(OH)_2$. In the experiments by Gjorv and Vennesland, addition of sea salts up to 4 percent did not lower the pH of the hydrated portland cement extract to below 12. Fortunately, for high-quality concrete, the penetration of magnesium ions is normally confined to a thin outer zone near the concrete surface, because due to the formation of a dense $Mg(OH)_2$ precipitate at the surface the permeability of concrete is considerably reduced. Hence, according to Gjorv and Vennesland, in such cases, the magnesium ions in sea water do not exercise any significant effect on reduction of alkalinity in high-quality concrete.

Similar observations are valid with regard to the effect of dissolved CO_2 on reduction of alkalinity of a hydrated portland cement paste. This explains how lack of adequate cover and lean concrete mixtures lead to corrosion of steel in concrete which has reduced in pH as a result of carbonation or magnesium ion attack on the hydration products of portland cement.

EFFECT OF ADMIXTURES ON PERMEABILITY OF HARDENED CEMENT PASTE

Permeability of concrete depends mainly on the permeability of the cement paste which, in turn, depends on its porosity and pore size distribution. With decreasing water-cement ratio, and with increasing degree of hydration of cement, both the volume and size of large pores are reduced, thereby causing a reduction of the permeability of the hardened cement paste. In unpublished work by Mehta and Manmohan (19), the influence of certain admixtures on reduction of volume of large pores was described, and a summary of the work is given here. The pore size distributions were obtained by mercury intrusion technique, and the permeability was determined by measuring the flow of pressurized water through cylindrical discs of hardened cement pastes.

In a study of the effect of water-cement ratio on pore-size distribution and permeability of portland cement paste, a good correlation was found between the permeability coefficient and volume of pores $> 1320 \text{ \AA}$. As long as a hydrated cement paste, regardless of the water-cement ratio and age of hydration, did not contain pores $> 1320 \text{ \AA}$, the permeability coefficient remained insignificantly low. This was essentially the case with pastes made with water-cement ratios of 0.5 or less, and the moist cured for 28 days or more. With increasing volume of pores $> 1320 \text{ \AA}$, the permeability coefficient was found to increase exponentially.

The effect of pozzolanic admixtures was found to depend on the reactivity of the pozzolan used. Addition of a 10, 20, or 30 percent ASTM Type F fly ash to portland cement, did not reduce the volume of large pores and the permeability of the cement pastes until after 90 days of moist curing. On the other hand, similar quantities of a highly reactive pozzolan, namely a rice hulls ash, caused significant reductions in the volume of large pores, already at 28 days. Similarly, as compared with a portland blast furnace slag cement containing 30 percent slag, the permeability of a 80 percent slag cement was considerably lower in spite of the higher total porosity of the latter, mainly because of difference in pore-size distribution.

Results of 2 percent additions of chemical salts namely chlorides of sodium, calcium, or magnesium on pore-size distribution are shown in Fig. 2. The cement pastes, containing the three chemical admixtures as well as the control portland cement paste, were made with 0.5 water-cement ratio. It is evident from the results of the mercury penetration analyses that the presence of chlorides significantly reduced the volume of large pores. The altered microporosity of the system may be associated with the

reticular structure of the calcium silicate hydrates which are reportedly formed in the presence of chloride ions. As expected, magnesium chloride had the greatest influence on the reduction of total porosity and permeability of the hydrated cement paste. This was probably due to precipitation of magnesium hydroxide in the pores.

CONCLUSION

Permeability is the most important characteristic determining the long-term durability of concrete exposed to sea water. Concrete made with high C_3A portland cement even, continues to have excellent service life if the permeability of the concrete is low. Among the methods to achieve low permeability in concrete structures are design of concrete mixtures having high cement content and low water-cement ratio, thorough consolidation, and prevention of cracking due to thermal gradient, mechanical loading, etc. Pozzolan additions to portland cement or use of blended cements containing large proportions of granulated blastfurnace slag improves the impermeability of concrete by reducing the volume of large pores in the hydrated cement paste. Preliminary research has shown that similar results can be achieved by addition of small amounts of chlorides, especially magnesium chloride, to portland cement.

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Forty cm mortar cubes made with different cements and three different cement contents, 300, 450, and 600 kg/m³, were exposed to sea water at La Rochell, southern France in 1904-1908. Reference: M. Regourd, Annales de L'Institute Technique du Batiment et des Travaux Publics, No. 329, June 1975 and No. 358, Feb. 1978.	After 66 years of exposure to sea water, the cubes made with 600 Kg/m³ cement, were in good condition even when they contained a high C₃A (14.9%) portland cement. Those containing 300 kg/m³ were destroyed, however, chemical resistance of the cement was of major importance for low cement-content cubes. In general, pozzolan and slag cements showed better resistance to sea water than portland cements. Electron micrographic studies of deteriorated specimens showed the presence of aragonite, brucite, ettringite, magnesium silicate hydrate, and thaumasite.
Eighteen 69x69x42 inch unreinforced concrete blocks, made with 6 different portland cements and 3 different concrete mixtures, partially submerged in sea water in Los Angeles in 1905. Reference: P. Mehta and H. Haynes, J. Str. Div. ASCE V. 101, No. ST8, Aug. 1975.	After 67 years exposure, the dense concrete (1:2:4) blocks, some made with 14 percent C₃A portland cement, were still in excellent condition. Lean concrete (1:3:6) blocks lost some material and were much softer. X-ray diffraction analyses of the weakened concrete showed the presence of brucite, gypsum, ettringite, and hydrocalumite. The cementing constituents, CSH gel and Ca(OH)₂, were not detected.
Precast reinforced concrete piles driven in 1912 to support a 2500-ft concrete wharf in the Los Angeles harbor. Reference: C.M. Wakeman et al. J. ACI, Proc. V. 54, 1958.	After 12 years, some piles started to crack longitudinally, beginning above mid-tide and continuing upward. Deterioration progressed rapidly, leading ultimately to crumbling and spalling. Concrete below the water-line was sound. Corrosion of the reinforcement by permeation of sea water through fissures produced by sulfate attack was suspected as the primary cause of spalled concrete above the water-line.
Concrete structures of the San Francisco Ferry Bldg., built in 1912. Type I portland cement with 14-17% C₃A was used. 1:5 concrete mixture contained 658 lbs/yd³ (395 Kg/m³) cement. (a) Precast concrete cylinders jacket for Pier 17 (b) Cast-in-place concrete cylinders for Pier No. 30 and No. 39 (c) Cast-in-place concrete cylinders and transverse girders for Pier No. 26 and No. 28. Reference: P.J. Fluss and S.S. Gorman, J. ACI, Proc., V-54, 1958.	After 46 years of service, (a) was found in excellent condition, and 90 percent of piles in (b) were in good condition. In (c), 20-30 percent of piles were attacked in tidal zone, and about 35 percent of the deep transverse girders had their underside and part of the vertical face cracked or spalled due to corrosion of reinforcement. Presence of microcracks due to deflection under load might have exposed the reinforcing steel to corrosion by sea water. Poor workmanship was held responsible for differences in behavior of concrete which was of the same quality in all the structure.

Table 1--Performance of concrete exposed to sea water in mild climate

History of Structures	Results of Examination
Many 20-50 year coastal structures were included in a 1953-55 survey of 431 concrete structures in Denmark. Among the severely deteriorated structures were the following in Jutland. (i) <u>Oddesund Bridge, Pier No. 7</u> History of structure indicated initial cracking of caissons due to thermal stresses. This permitted considerable percolation of water through the caisson walls and the interior mass concrete filling. General repairs commenced after 8 years service. (ii) <u>Highway Bridge, North Jutland</u> Severe cracking and spalling of concrete at the mean water level provided a typical hour-glass shape to the piers. Concrete in this area was very weak. Corrosion of reinforcement was everywhere and pronounced in longitudinal girders. (iii) <u>Groin 71, north barrier, Lim Fiord</u> Lean concrete blocks (370 lbs/yd³ cement) exposed to windy weather, repeated wetting and drying, high salinity, freezing and thawing, and severe impact of gravel and sand in the surf. Some blocks disappeared in the sea in the course of 20 years. Reference: "Durability of Concrete Structures in Denmark", Ph.D. Dissertation of G.M. Idorn, Tech. Univ. Denmark, 1967.	Of the coastal structures, about 40 percent showed overall deterioration, and about 35% showed from severe surface damage to slight deterioration. Examination of deteriorated concrete from the Oddesund Bridge indicated decomposition of cement and loss of strength due to sulfate attack below low-tide level and cracking due to freezing and thawing as well as alkali-aggregate reaction above high tide level. Reaction products from cement decomposition were arapontite, ettringite, gypsum, brucite, and alkali-silica gel. Examination of concrete piers of the highway bridge showed evidence of poor concrete quality (high w/c). Symptoms of general decomposition of cement and severe corrosion of the reinforcement were superimposed on the evidences for the primary deleterious agents, such as freezing-thawing and alkali-aggregate reaction. Examination of the severely deteriorated concrete blocks from Groin 71 showed very weak, soapy matrix with loose aggregate pebbles. In addition to the alkali-silica gel, the presence of gypsum and brucite was confirmed.
Along the Norwegian seaboard, 716 concrete structures were surveyed in 1962-64. About 60 percent of the structures were reinforced concrete wharves of the slender-pillar type containing tremie-poured underwater concrete. Most wharves had decks of the beam and slab type. At the time of survey, about two-third of the structures were 20-50 years old. Reference: "Durability of Reinforced Concrete Wharves in Norwegian Harbors", O.E. Gjorv, The Norwegian Committee on Concrete in Sea Water, 1968.	Below the low-tide level and above the high-tide level, concrete pillars were generally in good condition. In splashing zone, about 50 percent of the surveyed pillars were in good condition; 14 percent had their cross-sectional area reduced by 30 percent or more, and 24 percent had 10-30 percent reduction in area of cross section. Deck slabs were generally in good condition but 20 percent deck beams will need repair work because of major damage due to corrosion of reinforcement. Deterioration of pillars in the tidal zone was ascribed mainly due to frost action on poor quality concrete.
Pier No. 2 constructed in 1913, is supported by 1801 reinforced concrete piles of 24 inch cross section. The 1:1.5:3 concrete contained a 12 percent C₃A portland cement. Concrete in the tidal zone is protected with timber jackets. Reference: "Performance of Concrete in Sea Water-Some Examples from Halifax, Nova Scotia", D.C. Tibbetts, Proc. Thorvaldson Symp; 1968.	In 1930 after 17 years of service, about 50 percent of the surface area of the girders, beams, and columns above the timber jacketing as well as the underside of the slabs were found to be disintegrating in many places, exposing the reinforcing steel. This necessitated the repair of the 550,000 sq. ft. structure.

Table 2--Performance of marine structures in cold climate

Sea-water component which can enter into deleterious chemical reactions with hydrated portland cement.	Possible chemical reactions.	Physical effects associated with chemical reactions.
<u>Carbon Dioxide</u> Small quantities of dissolved CO_2, derived mainly from absorption of atmospheric CO_2, is always present in sea water. However, decaying vegetable matter can lead to substantially larger and harmful concentrations of dissolved CO_2, which are generally reflected by reduction of the sea water pH to values less than 8.	$\text{CO}_2 + \text{Ca}(\text{OH})_2 + \text{CaCO}_3 + \text{H}_2\text{O} \xrightarrow{\text{CO}_2} \text{Ca}(\text{HCO}_3)_2$ aragonite bicarbonate of calcium $\text{CO}_2 + [\text{Ca}(\text{OH})_2 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 18\text{H}_2\text{O}] + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaCO}_3 \cdot x\text{H}_2\text{O} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ gypsum $3\text{CO}_2 + 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{CaCO}_3 + 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ aragonite	Both calcium bicarbonate and gypsum are soluble in sea water. Loss of material and weakening or mushiness of hardened cement paste can therefore be associated with the formation of these compounds. Since all the hydration products of portland cement, including the calcium silicate hydrate, can be decomposed by carbonation reactions, permeable concretes in sea water containing larger than normal CO_2 concentration are likely to deteriorate.
<u>Magnesium Salts</u> Typically, sea water contains 3200 ppm MgCl_2 and 2200 ppm MgSO_4. Regarding cement hydration products, these magnesium salts, even in the small concentrations present, are considered harmful.	$\text{MgCl}_2 + \text{Ca}(\text{OH})_2 + \text{Mg}(\text{OH})_2 + \text{CaCl}_2$ brucite $\text{MgSO}_4 + \text{Ca}(\text{OH})_2 + \text{Mg}(\text{OH})_2 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ gypsum $\text{MgSO}_4 + [\text{Ca}(\text{OH})_2 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 18\text{H}_2\text{O}] + \text{Mg}(\text{OH})_2 + 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ettringite $\text{MgSO}_4 + [\text{Ca}(\text{OH})_2 + 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}] + 4\text{MgO} \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CaCl_2 and gypsum, being soluble in sea water, lead to material loss and weakening. Formation of ettringite is associated with expansion and cracking. It is reported that the conversion of $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ to $4\text{MgO} \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O}$ is associated with brittleness and strength loss.

Table 3--Decomposing action of sea water on the constituents of hydrated portland cement

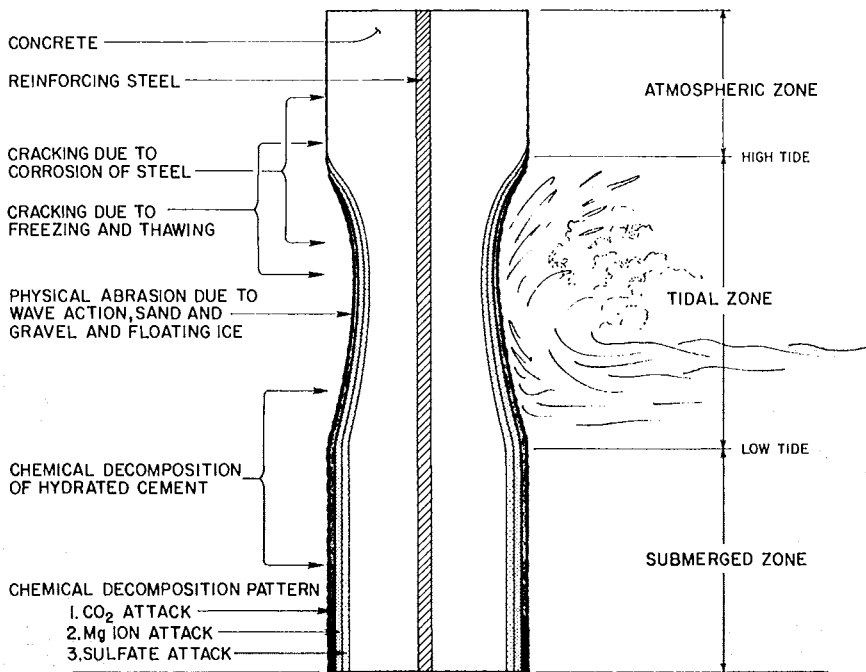


FIG 1. DETERIORATION OF A CONCRETE STRUCTURE IN SEA WATER

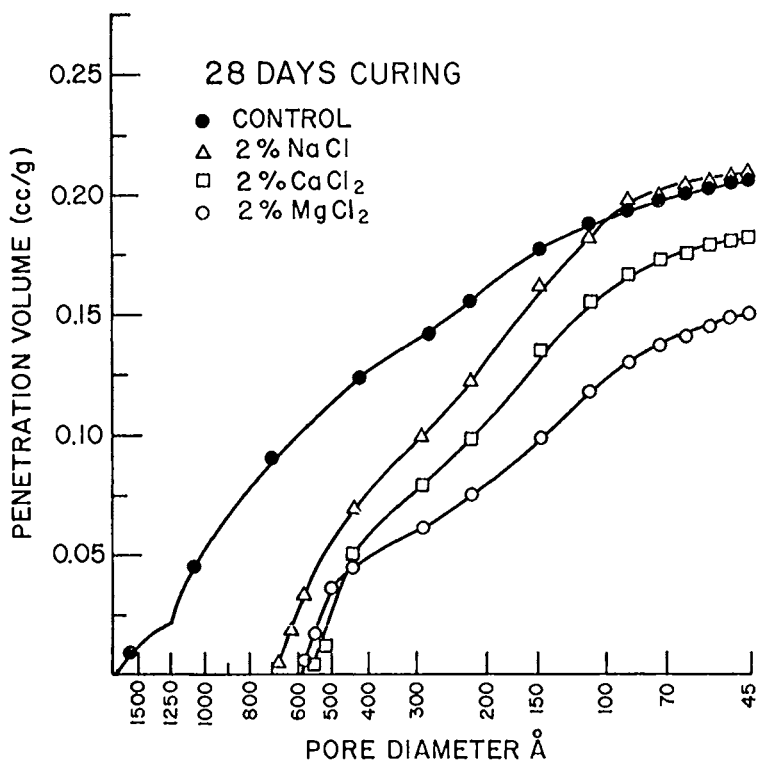


FIG. 2. EFFECT OF CHLORIDE ADDITIONS ON PORE SIZE DISTRIBUTION OF HYDRATED PORTLAND CEMENT PASTES

Permeability of Concrete in Sea Water

By Harvey H. Haynes

Synopsis: For fully hydrated concrete of excellent mix proportions, the minimum void volume is about 10%. The largest portion of the void volume is located in the cement paste which, viewed by itself as a solid matrix, has a minimum void volume of 28%. The size of the voids in the hydrated cement paste are sub-microscopic, but water molecules can move about and permeate the paste. Hence, the best concretes are permeable to water; however, the quantity of permeated water may be extremely small. Most of the published work on the permeability of concrete was based on using freshwater in the experiment. This paper summarizes some of the past work and presents results from a few studies on concrete exposed to seawater. One important new finding is that concrete permeated by seawater shows a decreasing permeability rate and it appears that permeability eventually stops. It is postulated that the reason for the decreasing permeability rate is the blocking of pore space by crystallization or precipitation of chemical products created by the interaction of seawater and hydrated cement.

Keywords: cement pastes; concrete durability; high-strength concretes; hydration; marine atmospheres; mix proportioning; permeability; porosity; sea water; voids.

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INTRODUCTION

For concrete in a marine environment, there appears to be a direct correlation between low permeability, high strength, and good durability. For this reason, concrete sea structures, such as offshore platforms and harbor structures, typically are built using high quality concrete. The American Concrete Institute has recently published a committee report on the Design and Construction of Fixed Offshore Concrete Structures (1) where the material recommendations call for, among other things, a water-cement ratio of 0.40-0.45 (by weight) and a minimum cement content of 356 kg/m^3 (600 lb/yd^3). Along with good concreting practice, this concrete should exhibit low permeability characteristics.

Most past work on permeability of concrete was on mass concrete for dam structures with its characteristic high proportion of large coarse aggregate, low cement content (about 150 kg/m^3 or 250 lb/yd^3) and water-cement ratios ranging from 0.50 to 0.70 (by weight)*. This paper discusses permeability of good quality structural concrete with higher cement content, lower water-cement ratios, and smaller coarse aggregate than the mass concrete.

Permeability of concrete, as in any material, is not so much a function of the amount of the void volume as it is a function of the size, distribution, and continuity of the voids. A discussion of the characteristics of the internal voids volume in concrete is necessary to understand permeability.

VOIDS IN CONCRETE

There are four types of voids in concrete: (a) air voids that occur inadvertently from mixing and placing concrete or intentionally by entraining about 2%-6% by volume of air as small bubbles to improve freeze-thaw characteristics; (b) sub-microscopic capillary voids that are created by the space originally occupied by the mix water; (c) sub-microscopic gel voids that are created as cement hydrates and "gel" is formed; and (d) voids of various sizes found in normal and lightweight aggregate particles. Other types of voids, which will not be discussed,

*W/C and A/C ratios are on a weight basis.

are internal cracks from humidity and temperature changes, voids under aggregate particles created by bleed water in concrete made with excessive water-to-cement ratio, and "honeycomb" voids from an overly dry or poorly compacted concrete mixture.

If we ignore the void volume in the aggregate, high quality concrete at a young age will have a total void volume about 20%-25% and at a mature age about 10%-15%. It is not possible for concrete to have a void volume less than about 10%. Thus, concrete will always have voids, and therefore, passageways exist for water to move through concrete.

Air Voids

Accidentally entrapped air voids have a size range up to several millimeters. They are typically isolated from other entrapped air voids and have little influence on the permeability of the concrete.

Intentionally entrained air voids have a size range from 0.07 to 1 mm (0.003 to 0.05 in.) in diameter and are distributed throughout the paste of the concrete. They are discrete, individual bubbles that are not interconnected with each other. It is reported that permeability is not increased by entrained air (2). The water-cement ratio can be reduced for air-entrained concrete while workability is held constant; this has the favorable effect of reducing the capillary void volume in the cement paste.

Capillary and Gel Voids

In a fresh cement paste mixture, the cement particles are rather evenly distributed due to electrostatic repulsion forces. If the water were removed, the pore spaces would be interconnected and would be capillary in size ranging from 8×10^{-6} mm to 13×10^{-3} mm diameter (3). For a paste of water-cement ratio of 0.40, the capillary volume would be about 56% of the total volume of the paste.

When the paste is freshly mixed, all the voids are capillary. Gel voids are formed as cement hydrates. Each cement grain reacts with water to form calcium-silicate-hydrate gel that surrounds the remaining unhydrated cement. With time, fiber-like chains of molecules, called fibrils, develop from the gel coating (4). The spaces between the fibrils are the gel voids.

The bulk volume of gel, after a cement grain is fully hydrated, requires 60% more space than the original size of the cement grain (5). The expansion moves into capillary space. Thus as hydration occurs, the capillary void volume decreases while the gel void volume increases. This is beneficial in reducing permeability because the gel pores are extremely small, typically from 1×10^{-6} mm to 8×10^{-6} mm diameter (3).

Theoretically, if the original water-cement ratio for the paste were 0.38, the entire capillary void volume could become filled with gel. The resulting volume of gel voids would be 28%.

A larger ratio of gel voids to capillary voids will aid in dramatically reducing permeability. In permeability tests there has been observed a relatively abrupt change in permeability behavior which is attributed to capillary voids being blocked-off by the formation of gel; in other words, the capillary system had become discontinuous. For cement pastes of water-to-cement ratio of 0.40, 0.50, 0.60 and 0.70 the time for this condition was estimated as 3 days, 14 days, 6 months, and 1 year, respectively (3).

Hence high quality concrete, which uses water-cement ratios between 0.40-0.45, should demonstrate low permeability rates even at young ages.

Aggregate Voids

About 75% by volume of concrete is composed of aggregate. Normal-weight aggregates consisting of gravel or crushed rock and lightweight aggregate are both used in marine concrete. For normal-weight aggregates the permeable pore space within the aggregate particles can have a void volume from nearly 0 to 20%, most typically from 0.5 to 5%. The pore size is relatively large because the permeability is similar to that of cement paste having a void volume of 50% (6).

Lightweight aggregate particles have a void volume from 30 to 60%. The voids are relatively large and interconnected so there is little resistance to water movement within the individual particle.

The author had occasion to test an all-lightweight-aggregate concrete hollow sphere under hydrostatic pressure at 13.8 MPa (2,000 psi). The purpose was to determine the watertightness of the concrete wall of the sphere. The sphere was 406 mm (16 in.) in outside diameter and 76 mm (3 in.) in wall thickness. The cement content was 460 kg/m³ (774 lb/yd³) and, using saturated aggregate, the free water-cement ratio was 0.43. The compressive strength was 41.4 MPa (6,000 psi) at the time the sphere was tested (at an age of 172 days of continuous fog curing). The sphere was subjected to external hydrostatic pressure of 6.9 MPa (1,000 psi) (using fresh water) for 7 days and no water collected on the interior. The pressure was raised to 13.8 MPa (2,000 psi) and maintained for 30 days. After the 7th day at 13.8 MPa (2,000 psi), water started to collect in the cavity of the sphere and totalled 16 ml by the 30th day.

The rate of water permeation was similar to that of a hollow mortar sphere of the same size containing normal weight aggregate (maximum size no. 4), cement factor of 490 kg/m³ (825 lb/yd³), and water-cement ratio of 0.55 (7).

Tests of lightweight aggregate alone showed that 1.7 MPa (250 psi) hydrostatic pressure completely saturated the particles after 1 day of exposure (8). Hence, the aggregate did not contribute to the watertightness of the concrete, the watertightness came from the cement paste surrounding each aggregate particle.

PERMEABILITY

Past work was limited to permeability of neat cement paste and concrete to freshwater (6, 9-13). Typically, the tests used cylinder or disc-shaped solid specimens with the water directed axially through the material. Various surface preparation methods were used to try to obtain representative concrete at the high pressure face. The water was either de-aerated, filtered, or distilled.

Permeability results were expressed as a coefficient of permeability, K, given by Darcy's equation for laminar flow through a porous medium

$$\frac{dQ}{dT} = K A \frac{\Delta h}{L}$$

where dQ/dT = rate of flow of water (m^3/sec)

A = area perpendicular to flow of water (m^2)

Δh = drop in hydraulic head through the sample (m)

L = length of path of water flow (thickness of sample) (m)

The coefficient of permeability, K, has units of velocity (m/sec).

Darcy's equation applied well to concrete when a condition of steady flow was attained.

In tests, steady flow occurred between a few hours to 10 days depending on test conditions, such as specimen thickness, pressure head, water-cement ratio, and other factors.

Although few tests were conducted on high quality concrete, the results from cement pastes having low water-cement ratios can be assumed representative of quality concrete. Powers, et al. (6) conducted a large number of tests on cement pastes. Basically their findings showed that the water-cement ratio was the controlling parameter. Figure 1 shows permeability as a function of water-cement ratio for mature cement paste. At the water-cement ratio of 0.40, K was about 1×10^{-14} m/sec.

Naturally, the pastes with a higher water-cement ratio had an increased portion of the total void volume as capillary voids. As stated earlier, the capillary voids essentially control the permeability. Figure 2 shows permeability as a function of

capillary void volume. At low capillary void volumes, the permeability coefficient approaches that of cement gel which is about 7×10^{-16} m/sec (14).

Some permeability results on concrete exposed to seawater are available from Stachiw and Mack's work (7) on hollow spheres, 406 mm (16 in.) OD and varying wall thicknesses of 25, 51, 76, and 102 mm (1, 2, 3, and 4 in.). The normal-weight aggregate concrete mix had a cement factor of 490 kg/m³ (825 lb/yd³), water-cement ratio of 0.55 and maximum aggregate size of 5 mm (0.2 in.). An external pressure of 13.8 MPa (2,000 psi) was maintained on the spheres from 4 to 24 days before water appeared in the interior cavity which was maintained at atmospheric pressure. For spheres of progressively greater wall thicknesses, the flow rates, averaged over 5 days, were presented as 1.4, 0.535, 0.156, and 0.038 ml/hr; these yielded K values of 1.8, 1.9, 1.2 and 0.6×10^{-14} m/sec. These values were similar to that found by Powers (6) for cement pastes having a water-cement ratio of 0.40.

Experimental Tests in Ocean

Permeability results on concrete exposed to seawater have been obtained from an on-going test of hollow concrete spheres exposed to deep ocean conditions (15,16). In 1971, 18 spheres, each 1,676 mm (66 in.) OD by 104 mm (4.12 in.) wall thickness, were placed in the Pacific Ocean. Each sphere is individually anchored near the seafloor. The spheres are located at various water depths ranging from 550 to 1,500 m (1,800 to 5,000 ft). Sixteen spheres were of unreinforced concrete; eight of these were coated on the exterior with a phenolic compound to act as a waterproofing agent and eight were left uncoated. The remaining two spheres were lightly reinforced with 13 mm (0.5 in.) diameter steel bars. Half of each of the reinforced spheres was coated with the waterproofing agent. The purpose of using reinforced spheres was to determine whether corrosion problems exist in the deep ocean.

The concrete mix had a Type II portland cement content of 435 kg/m³, water-cement ratio of 0.41, sand-cement ratio of 1.85, and coarse aggregate-cement ratio of 2.28. The maximum size aggregate was 19 mm (0.75 in.). The compressive strength at 28 days was a nominal 55 MPa (8,000 psi).

Annual inspections of the spheres in situ, using either manned or unmanned submersibles, gathered data on the permeability of the spheres. The spheres are positively buoyant by approximately 450 kg (1,000 lb) and tethered about 10 m (30 ft) off the seafloor by a 57 mm (2.25 in.) diameter chain. Figure 3 shows a sphere in place at 850 m (2,800 ft) after 1 year exposure. As a sphere takes on water by absorption, initially, and then by permeation of water through the wall into the interior, the sphere becomes heavier and loses buoyancy. Therefore, fewer chain links are held off the seafloor. Thus, by counting the

links of chain off the seafloor, permeability data were obtained. One chain link represents 14 liters of seawater "taken-on" by a sphere.

Data are available over a period of 6.4 years. Seven inspections have been made, the most recent in March 1978. During each inspection, not all the spheres were inspected. Hence some spheres have been inspected more frequently than others.

After five years in the ocean, three spheres were retrieved. Two of the spheres had a waterproof coating and were retrieved from the depths of 803 and 957 m (2,630 and 3,140 ft). The third sphere was uncoated and was retrieved from 850 m (2,800 ft) (Figure 4). The interior of each of the spheres was tapped to determine the actual quantity of permeated water. The coated spheres were dry on the interior which was the expected result. The uncoated sphere had 39 liters of water on the interior; from the inspection data (chain link count), the volume of permeated seawater had been predicted to be 35 liters.

The inspection data (counting chain links) gave total seawater intake by the spheres. The weight of seawater absorbed by the concrete was estimated as 3% by weight. This value was determined for identical concrete by extrapolating data obtained at 168 m (550 ft) pressure head for 86 days (17) to a time period of 3 years when absorption appeared complete.

Figure 5 shows total water intake as a function of time for the coated and uncoated spheres. The coated spheres had not absorbed enough water to even saturate the concrete. The waterproof coating had "pinholes" (or "fish-eyes") so the barrier was not perfect. Water had access to the concrete, but these local areas of infiltration must have become watertight by themselves. It appears that this occurred before the first inspection at 1/2 or 1 year in the ocean.

The uncoated spheres absorbed enough seawater to saturate the concrete and then had some seawater permeate the wall to the interior. In general, the uncoated spheres also stopped taking on seawater before the first inspection. Some undefined mechanism made the concrete watertight; this topic will be discussed later.

Data are available on the permeability of hollow concrete spheres to seawater for time periods from 0 to 42 days (18). These data are from two spheres tested in a pressure vessel. The spheres were initially subjected to water pressure on the interior and exterior to accelerate water adsorption by the concrete. A pressure head of 340 m (1,125 ft) was maintained for 7 days. The test set-up was then arranged so that the interior volume of a sphere, which was filled with water, was vented to the atmosphere. The water flowing out of the sphere was collected. During pressurization the water outflow represented instantaneous deformation of the sphere. When the pressure was held constant

the water outflow was a measure of creep deformation and permeated seawater. After about 10 days the water outflow was principally a measure of permeability.

Figure 6 shows the cumulative quantity of permeated water, Q_p , as a function of time for the two spheres. One sphere was subjected to a pressure head of 768 m (2,500 ft) for 21 days and the other sphere 1,145 m (3,750 ft) for 42 days. The decrease in permeability with time is quite evident from the changing shape of the curves.

Darcy's equation can be applied to spherical test specimens. The permeability coefficient, K , can be expressed as:

$$K = \frac{Q_p t}{T A_s h}$$

where Q_p = quantity of permeated seawater (m^3)
 T = time (sec)
 t = wall thickness (in.)
 A_s = interior surface area (m^2)
 h = pressure head (m)

Darcy's expression applies to steady flow conditions which the spheres did not exhibit. However, for comparison purposes the slope of the curve can be used to represent the early-age permeability coefficient for the concrete. For sphere CWL-6 under 1145 m (3,750 ft) pressure head, K was 6×10^{-14} m/sec at 10 days, 3.5×10^{-14} m/sec at 20 days, and 2×10^{-14} m/sec at 40 days. These values compare favorably with the results from Powers who found $k = 1 \times 10^{-14}$ m/sec for cement paste having a water-cement ratio of 0.40.

Discussion of Test Results

The actual cause for the self-waterproofing behavior of concrete exposed to seawater has not been experimentally determined. There are a few possible explanations for this behavior:

1. The cement continued to hydrate and gel filled the capillary voids. Logically, some of this mechanism occurred but, as shown in Figure 6, the actual rate of permeability decrease was too rapid for this to be the only explanation. The spheres in Figure 6 were a year old when the test was conducted so the cement was well hydrated before the test began.

2. Micro-organisms in seawater "plugged" the voids. This mechanism is unlikely because of the extremely fine sizes of voids that need to be plugged. The smallest micro-organisms are about 3×10^{-4} mm where small gel voids are about 1×10^{-7} mm in diameter.

3. Chemical reaction between the ions in seawater and the hydrated cement produce crystallization or precipitation products that reduce the permeability. This mechanism has credibility and is supported by several observations noted in the literature.

Griffin and Henry (19) used seawater and man-made saltwater as the mix water to make concrete and then studied the water vapor transmission of the concrete. The test set-up had one face of concrete discs exposed to 100% relative humidity while the other face was at 20, 50 or 75% relative humidity. For concrete having a water-cement ratio of 0.70 and a specimen thickness of 75 mm, the water vapor transmission values were reduced by about 50% for concrete made with seawater as compared to concrete made with fresh water. Also an interesting observation was made, that is, salt whiskers were formed on the low relative humidity face of the concrete.

Stachiw and Gray (20) conducted exploratory tests on hollow concrete spheres, 406 mm (16 in.) OD by 25 mm (1 in.) wall thickness, subjected to hydrostatic loading. One particular specimen was tested for seawater permeability. It was exposed to 5.2 MPa (750 psi) of pressure for 20 days, and after the 11th day water permeated the wall and showed a flow rate of 2.5 ml/hr, which represents a permeability, K , of 5×10^{-14} m/sec. The sphere was removed from the pressure vessel for inspection and "dried out" (presumably at 20% relative humidity) for 20 days and then replaced in the pressure vessel and pressurized to 10.3 MPa (1,500 psi) for 7 days during which no water permeated the wall. The sphere was again removed from the pressure vessel for inspection and dried out for 9 days. It was then subjected to 13.8 MPa (2,000 psi) of pressure for 8 days without any water permeating the wall. The sphere was subsequently imploded at 17.2 MPa (2,500 psi). After the first cycle of pressure, the salinity of the water on the interior of the sphere was found to be about 20% lower than the exterior seawater. Were some of the ions in seawater concentrated to where crystallization occurred or did some of the ions react chemically with the cement to form precipitates?

Table 1 shows the major ions that are found in typical open ocean seawater. Chlorides are the major ion in seawater; however, there are numerous other ions also present.

In a recent paper (21), Powers noted that experimental results from permeability tests using freshwater were affected because the presence of sodium and potassium ions had a large influence on the mobility of water in small pores.

In seawater, sodium ions represent about 31% of the total ions, and potassium ions about 1%.

Gjorv, et. al., (22) conducted electrical resistivity tests on concrete exposed to seawater. For one type of test, the resistivity increased during a test period of 20 weeks which

indicated a progressive reduction in permeability. When a sample had the exterior surface cut away (1 mm removed) the resistivity returned to the original value, thus indicating that a surface phenomenon was present. It was suspected that brucite, $\text{Mg}(\text{OH})_2$, was formed from chemical action between magnesium ions in seawater and concrete. Brucite is rather insoluble in water and could have precipitated to block the pores in the surface layer.

The present author took samples of concrete from the uncoated ocean sphere and used an X-ray diffractometer to try to identify the presence of brucite. Brucite was not detected in the concrete, even in samples from the outside 1 mm of the wall.

Perhaps other products were blocking the pores. Gjorv (22) noted that other precipitates could be formed, for example tricalcium chloroaluminate and tricalcium chloroferrite (known as Friedel salt in their solid solution). Calcium, aluminum and iron ions are available from the cement, chloride ions are abundant in seawater.

All these observations lead one to postulate that chemical reactions within the concrete in the presence of seawater are responsible in some way for the reduction and eventual stoppage of permeability in the ocean spheres. This is not to say that all concrete exposed to seawater will behave in the same manner. The spheres in the ocean and in the laboratory pressure vessels were under high hydrostatic pressure which placed the concrete in a state of high multiaxial compressive stress. In addition, the spheres in the ocean were in a low temperature environment of about 5°C. Further studies need to be conducted under other stress and environmental conditions. For example, solid concrete elements exposed to harbor environmental conditions.

Beneficial effects should not always be expected from seawater in contact with concrete. Experience has shown that seawater can act against concrete and cause a breakdown of the material. This has been attributed to concretes of too high a porosity (23, 24).

If future research studies establish that permeability is a key to concrete's durability in seawater, then a major step forward in concrete technology will have been made. The test results from the concrete spheres in the ocean have shown that the potential exists for concrete to become watertight. The ability to understand and control this mechanism would significantly increase the long-term resistance of concrete to the marine environment.

SUMMARY

Permeability of concrete exposed to seawater has been found to exhibit a different behavior than that of concrete exposed to freshwater. In freshwater, steady permeability rates were obtained, but in seawater the permeability rates decreased with

time. Although results were limited, the specimens were large-scale and exposed in the ocean and also to real seawater in the laboratory. The decreased permeability rate may be due to chemical reactions (between the ions in seawater and the hydrated cement) that produce crystallization products or chemical compounds that precipitate to block the pores in concrete.

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Table 1. Major Ions Found in Seawater^a

Name	Chemical Form	Amount % by Weight
Chloride	Cl ⁻	19.35
Sodium	Na ⁺	10.76
Sulfate	SO ₄ ⁼	2.71
Magnesium	Mg ⁺⁺	1.29
Calcium	Ca ⁺⁺	0.41
Potassium	K ⁺	0.39
Other		<u>0.23</u>
TOTAL		35.14

^aHandbook of Ocean and Underwater Engineering, McGraw-Hill Book Company, 1969, p 1-17.

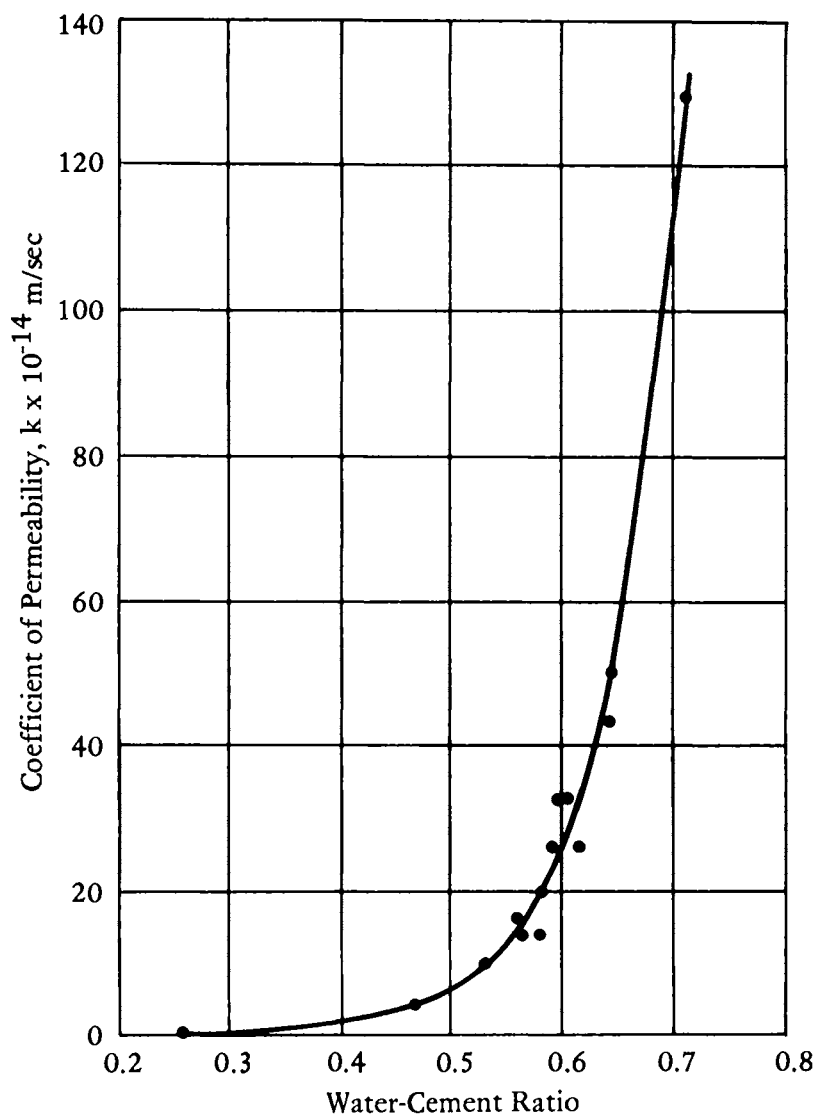


Figure 1. Relation between permeability and water-cement ratio for mature cement pastes (93 percent of cement hydrated) (Ref 6).

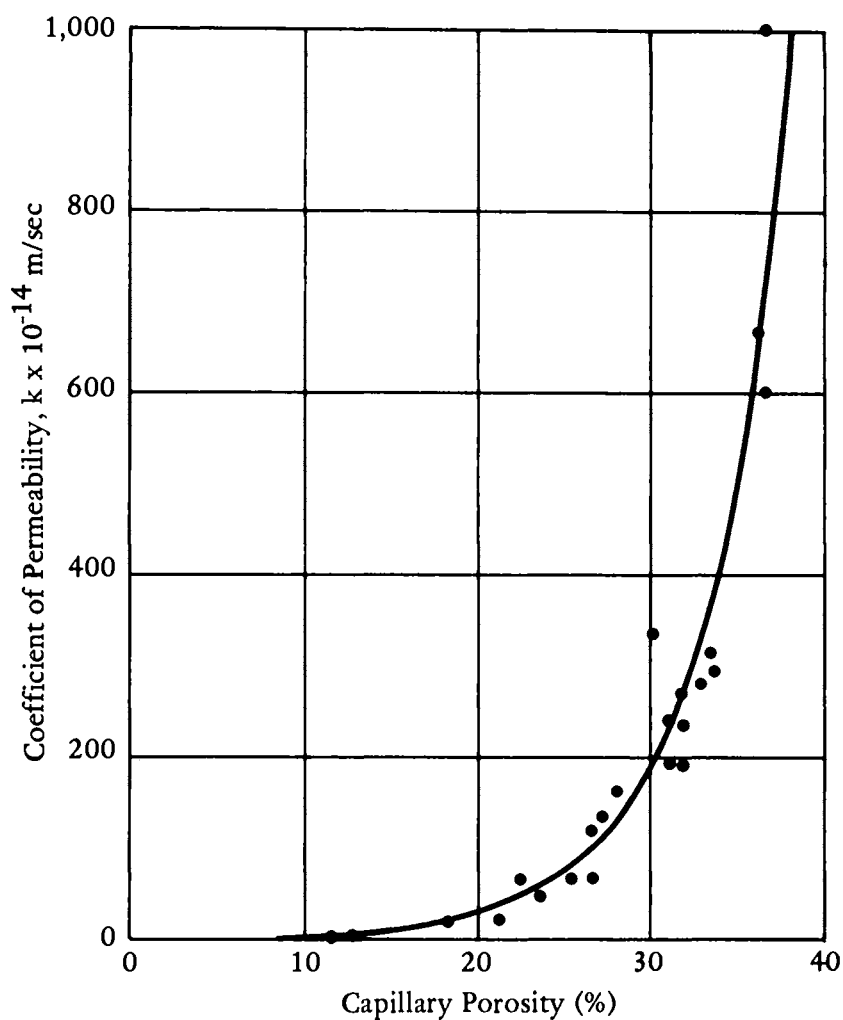


Figure 2. Relation between permeability and capillary porosity of cement paste (Ref 14).

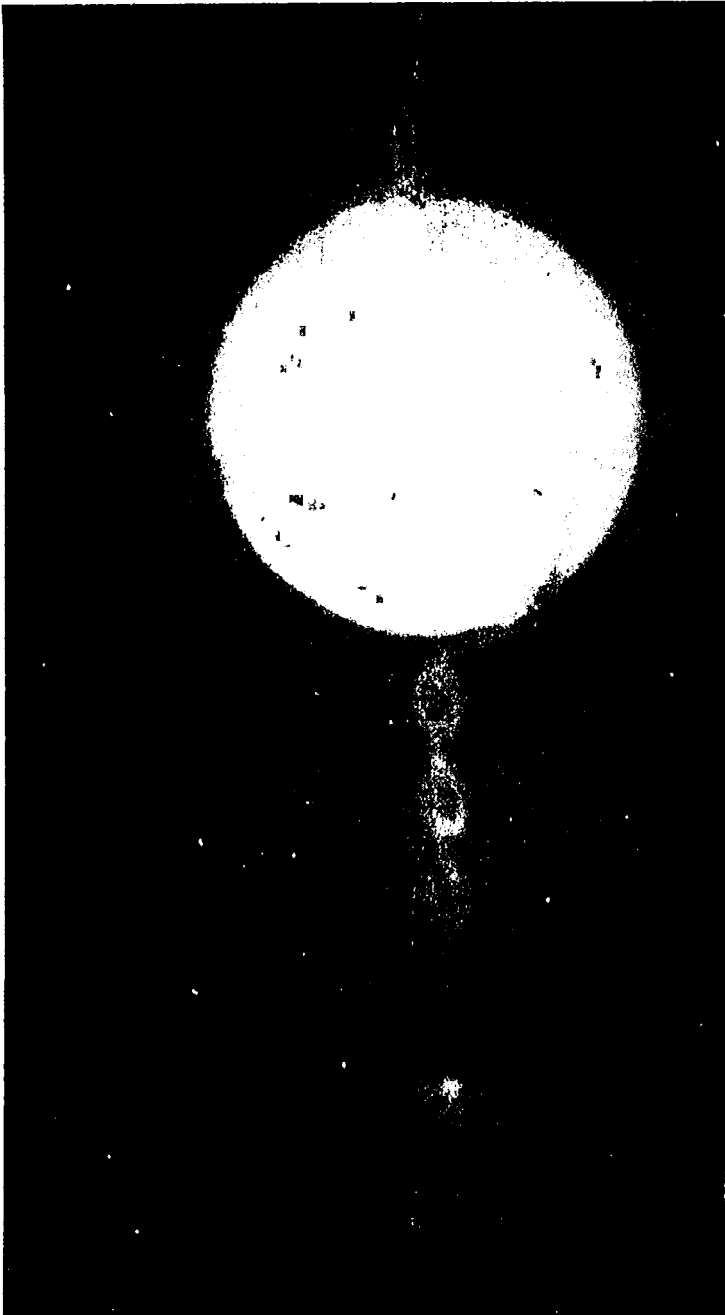


Figure 3. Uncoated concrete sphere, 1,676mm OD by 104mm wall thickness, tethered off the seafloor at 850m.



Figure 4. Uncoated concrete sphere retrieved from 850m depth after 5 years in the ocean.

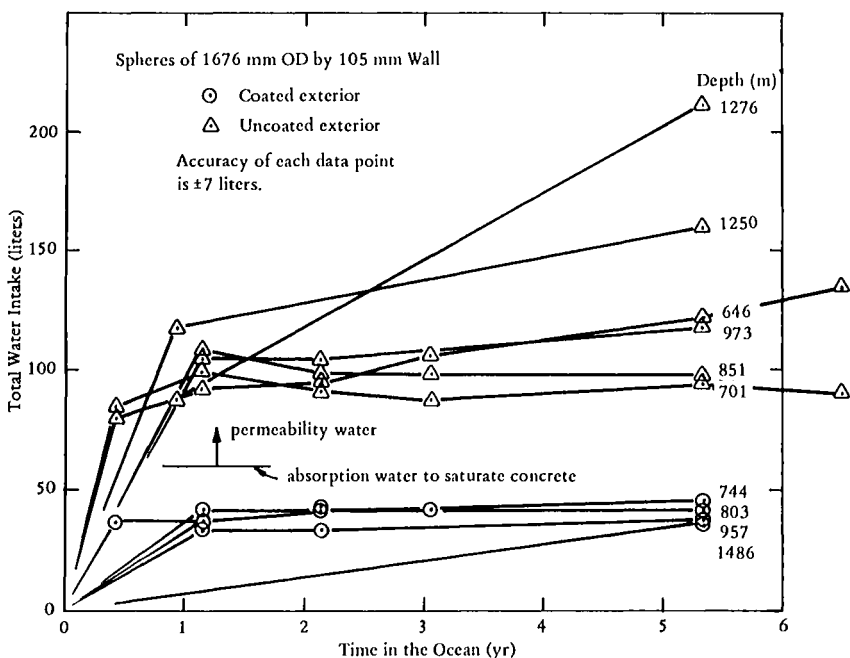


Figure 5. Total water intake (absorption and permeability) for spheres in the ocean (Ref 16).

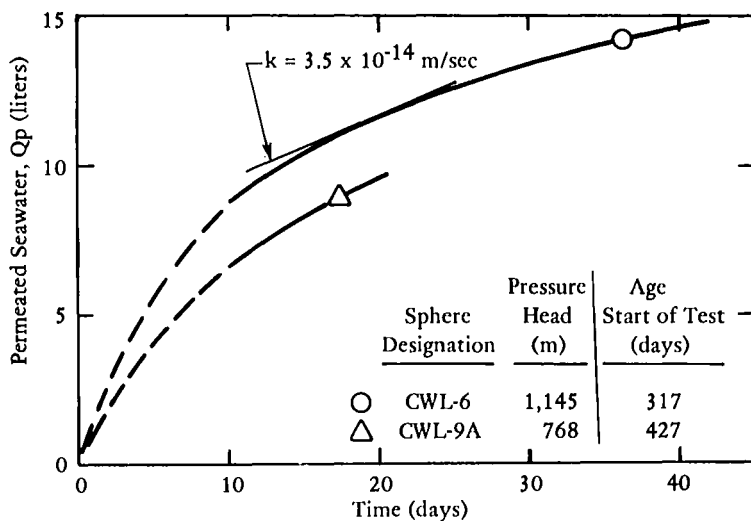


Figure 6. Permeability of concrete spheres to seawater at early exposure days (after Ref 18).

Mechanism of Sea Water Attack on Cement Mortar

By M. L. Conjeaud

Synopsis : Five kinds of commercial Portland cements and one C_3S sample were used for the study. The test prisms were made of mortar with a cement-sand ratio of 1 : 3 and a water-cement ratio chosen in order to give an ASTM flow of $110 \pm 5 \%$. After 28 days water curing, the test prisms were immersed in seawater, then, at fixed periods, up to 3 years, they were investigated by means of strength tests, chemical analysis, X-ray diffraction and scanning electron microanalysis. Results obtained show that SO_3 and especially Cl diffuse rapidly in the cement mortars, but their penetration is soon slowed down by the formation of an almost impermeable $Mg(OH)_2$ and/or aragonite layer on the mortar. It is postulated that this formation of a protective layer which occur with all the cements investigated is the main reason why immersed cement mortars are little attacked by seawater, even when the cement is C_3A -rich, whereas attack is greater at tide level where the $Mg(OH)_2$ and/or aragonite layer is subject to cracking.

Keywords: chemical analysis; corrosion mechanisms; C_3A ; C_3S ; electron microscopy; hydration; magnesium hydroxides; marine atmospheres; mortars (material); portland cements; sea water; water-cement ratio; x-ray diffraction.

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INTRODUCTION

The corrosion of concrete by seawater and its progress with time is a problem of great importance. Knowledge of this process for designing concrete structures of predictable service life is highly desirable. But the corrosive attack of mortars and concrete by seawater is a very complex process involving interrelated factors (mechanical, physical and chemical). Consequently, although extensive studies have already been reported, there are still many features of the mechanism of seawater attack on concretes which remain obscure or debatable.

The purpose of this investigation is to elucidate the microstructure of mortars affected by seawater under experimental conditions as near as possible to those encountered in the field, and this is done in correlation with strength loss tests. Most studies to date, have been, either technical studies, based on observation of external visual appearance and measurements of the expansion coefficient and/or strength of concretes or mortars after immersion in seawater (1 – 7), or scientific studies involving observation of hardened cement pastes or mortars without strength measurements (8 – 19).

EXPERIMENTAL

Tests procedure

The corrosive effect of seawater was tested by an accelerated method developed and now in general use in our central laboratory since 1968 (20). Acceleration of corrosion is obtained by using test prisms of high surface/volume ratio. The seawater is usual artificial seawater (Table 1) at 20°C. These conditions were maintained throughout, in order to avoid deviating too far from field conditions with the attendant risk of reaching false conclusions.

Test specimens were 2 x 2 x 10 cm mortar bars with a cement-sand ratio of 1 : 3 and a water-cement ratio chosen in order to give an ASTM flow of 110 ± 5 %. Sand was P 15-403 French Specification standard sand. After air curing at 98 % R.H. for one day at 20°C and water curing for 27 days at 20°C, the prisms were placed vertically in the corrosive solution. They were half immersed, the solution at 20°C being kept at constant level and renewed each month. After selected times of exposure, two prisms were sawn in half at the solution/air interface and compressive strengths of immersed and emergent halves measured and compared with the compressive strength of 20°C water-cured reference prisms.

Materials

Four brands of industrial Portland cements, one brand of type V cement, and a synthetic C_3S sample have been used for the investigations. Their characteristics are given in Table 2.

Exposure times

All specimens were tested at 1, 3, 6, 9, 12, 18 months, 2 and 3 years. Much shorter exposure times (2, 7, 14 and 28 days) were also studied for one cement (cement C).

Chemical and physical analysis

For all test specimens, the sample used for strength measurements was immediately crushed and washed with isopropyl alcohol in order to stop the hydration. Then after passing through a 100 μm sieve to remove as much sand as possible, the enriched samples were examined by X-ray diffraction (XRD) for identification and amounts of hydrates formed, and by chemical analysis for total penetrated Cl and SO_3 . A problem arose in obtaining fully quantitative results, due to the sand remaining in the sieved samples. However, using a correction procedure, based on quartz (for XRD) and insoluble residue (for chemical analysis) measurements, semi-quantitative results could be obtained.

At each age, a third sample, identical to the ones used for strength measurements is taken for observing microstructure of attacked cement mortar by scanning electron microscopy (SEM), measuring diffusion of Cl and SO_3 , and analysing the phases formed by energy-dispersive X-ray (EDX) microspectrometry. The procedure for measuring Cl and SO_3 diffusion is to scan jointed successive 1.3 mm wide layers starting at the external face of the mortar prism and register their X-ray spectra. From such spectra, the relative proportion of Ca , Al , Si , Fe , Cl , S present in the analysed layer can be computed. Allowance for sand contamination when calculating the true amount of Cl and SO_3 present, was based on the assumption that no leaching of CaO occurs (which, in disagreement with results of other workers (21, 22), was true even at the longest ages, as checked by chemical analysis) and that all Ca present comes from the cement. This second hypothesis is not exactly true since the sand used contains some calcite, but this should not affect the relative concentrations obtained.

RESULTS

Compressive strength

Compressive strengths of all specimens are given in Table 3. They show a very large variation with time, but, checking the reproducibility of the measurements, it was found out that a very large scatter occurs for all strength measurements made on specimens exposed to seawater, especially on immersed halves. The standard deviation is approximately 6 MPa for emergent halves, approximately 8 MPa for immersed halves, whilst it is approximately 3 MPa for water-cured specimens. We have no actual explanation for this at present, but it is of concern to draw conclusions

out of Table 3.

First, according to the scatter, it has to be said that no significant compressive strength losses were detected for the emergent halves of any cement studied, even after 3 years of exposure to seawater.

Compressive strength losses of immersed halves are shown in Fig. 1. They are measured by the ratio R_i/R_o , where R_i and R_o are the compressive strengths reached by the mortar in seawater and ordinary water respectively. Even for these immersed halves, strength losses are relatively low compared to what we obtained under the same conditions but exposed to $MgSO_4$ containing solutions (23). However, some significant differences are observed after two years of exposure, but they cannot be easily correlated with the cement composition. As a matter of fact, relatively large differences occur between cements very similar in composition (as A or F and C), whilst no significant discrepancies are observed between C_3S and cement C (13,6 % C_3A) mortars.

Hydration

Because of the high stability of emergent halves, only the immersed halves were studied by chemical analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray microanalysis (EDX).

The average amounts of Cl and SO_3 (additional to that present in the original cements) which diffused into the mortars are shown in Fig. 2. They are expressed in percent of the weight of cement. The data show, which is agreement with previous studies (12, 15) that, in average, much more Cl than SO_3 has penetrated. But as in the case of strength measurements, a considerable scatter in the results is observed, which remains to be explained. Nevertheless, the results are interesting for they show quite a sharp initial increase in the Cl and SO_3 concentrations followed (after about 1 month for SO_3 and about 3 months for Cl) by a marked deceleration in the rate of penetration, as if after a certain age, penetration of ions is hindered.

The Cl and SO_3 diffusion data, obtained by the EDX scanning technique described previously, is given in Fig. 3 for different cements and various times of exposure. It shows that the rate of diffusion is higher for chloride than for SO_3 . It can be seen for instance that penetration depth for cement C mortar, after 14 days exposure to seawater, is approximately 5 mm for Cl and approximately 2 mm for SO_3 . This is in agreement with Kalousek results (12) obtained by the sectioning technique. But after about one month exposure, SO_3 and Cl ions have reached the middle of the mortar bar (that is 10 mm depth) and with continued exposure the concentration gradients of Cl and SO_3 from the surface to center of the mortar bars diminishes for all cements used. For the longest exposure and with most cements, it even seems to reverse for Cl, the highest Cl concentration observed being located toward the middle of the bars. These data strengthen and complement the chemical results. Everything seems to happen as if, after about 3 months, no more Cl and SO_3 ions could penetrate from the seawater into the mortar bars.

Hydration kinetics of seawater immersed halves of mortars followed by XRD are summarized in Fig. 4. The study was made by comparison with the hydration kinetics of the water-cured reference mortars. It shows :

- the rate of calcium chloroaluminate ($C_3A \cdot CaCl_2 \cdot 10 H_2O$) formation.
- the amount of extra ettringite formed from seawater, measured by subtraction with respect to the water-cured samples. In most cases, for long hydration times the amount of ettringite found, both in seawater and ordinary water is reduced and some calcium monosulfoaluminate ($C_3A \cdot CaSO_4 \cdot 13 H_2O$) is detected. In order to take this into account, an asterisk is shown on the diagram next to the corresponding ettringite data.
- the amount of $Ca(OH)_2$ which has been consumed in seawater with respect to ordinary water. Here, it has to be recorded, as noted earlier, that no leaching of CaO occurred even after 3 years of exposure to seawater.
- the compressive strength losses.

The most striking feature of these data is the strong deceleration of all phenomena after about 1 – 3 months exposure to seawater. Nevertheless, the deceleration rate and the levels reached are not the same for all cements studied.

Cements A and F which have deteriorated most, show the highest amounts of calcium chloroaluminate, extra ettringite, and consumed $Ca(OH)_2$. Moreover, for cement F, consumption of $Ca(OH)_2$ is slowly increasing from 1 to 3 years exposure. No parallel increase of calcium chloroaluminate or ettringite is detected but a significant increase of the average Cl and extra SO_3 content is observed (Fig. 2).

Despite its very small strength loss, cement C shows almost as high an amount of calcium chloroaluminate and extra ettringite formed as cements A and F. In the same way, the average penetration of SO_3 and Cl is only slightly lower.

Cement B shows a much lower amount of calcium chloroaluminate formed, but not so low extra ettringite, and these results are in agreement with the average Cl and extra SO_3 reached after 3 months exposure.

Cement D shows about the same amount of calcium chloroaluminate formed as cement B but much less extra ettringite, although the average SO_3 penetration is equivalent for the two cements. This is probably due to the fact that cement D contains no C_3A and Fe – ettringite being poorly crystallised (12) is underestimated by XRD.

For cement E (C_3S), the average SO_3 penetration is as high as for the five industrial cements and the average Cl penetration is lower but still not negligible (approximately 2 % Cl after 3 months exposure). Nevertheless, in spite of the small amount of C_3A present in the sample, neither ettringite nor calcium chloroaluminate could be detected by XRD. On the other hand, neither gypsum nor calcium chlorosilicate was detected either (but gypsum and calcium chlorosilicate were observed by SEM).

Results for cement C at early ages are given in Fig. 5. It can be seen from this figure that strength loss reaches its maximum after about 1 month exposure whilst different maxima are observed for Cl and SO_3 diffusion. SO_3 diffusion reaches its maximum after a few days exposure and this is in agreement with the amount of extra ettringite observed by XRD. By contrast, Cl diffusion continues to increase up to 3 months, in step with the calcium chloroaluminate formed. $\text{Ca}(\text{OH})_2$ consumption has an intermediate maximum at about 14 days exposure.

Microstructure

X-ray maps of the various elements present in the mortars (an example is given in Fig. 6) show the presence of a Ca – rich deposit on the surface of the mortar prisms, and, just below it, the formation of a Mg-rich layer. The Ca-rich deposit is aragonite, and the Mg-rich layer is $\text{Mg}(\text{OH})_2$ (brucite) as checked by XRD. Neither Cl nor SO_3 are detected in aragonite and brucite. They are found below the brucite layer, in the interior of the mortar.

The brucite layer forms very early. It is observed after two days exposure, which is our earliest test age. Its thickness varies from one sample to another, from one side of a sample to another and even from place to place on the same side, but on an average it is about 20 – 50 μm (more rarely 100 μm) for C₃S and Type I cements and it does not increase with the time of exposure. By contrast, the brucite crystallisation improves significantly with time (Fig. 7). On Type V cement mortars, thinner brucite layers are observed. It is probably due to the smaller amount of $\text{Ca}(\text{OH})_2$ contained by these mortars.

Before exposure to seawater, the mortar prisms being water-cured are covered by a calcite deposit (Fig. 8 a). In seawater, due to the Mg^{++} ions in solution, calcite is unstable with respect to aragonite (24, 25, 26). An aragonite deposit will then form. The dissolution of calcite and the formation of aragonite could be followed. After two days exposure, calcite crystals start to dissolve, and elongated fish like aragonite crystals are detected (Fig. 8 b). After 7 days of exposure needle like aragonite urchins start to appear in the middle of dissolving calcite (Fig. 8 c). After 14 days, most calcite has dissolved and the brucite layer becomes visible, whilst the aragonite urchins which have grown bigger and more numerous are dispersed in this layer (Fig. 8 d). For longest exposures, after about 3 months, the aragonite urchins link up together and form an irregular but continuous deposit on top of the brucite layer (Fig. 9).

The thickness of the aragonite deposit, including the needle urchins, may reach about 300 μm after two years exposure to seawater, but it is very variable and deposits much thinner are observed for long-term exposures. The observed thicknesses of the aragonite deposits are equivalent for all cement studied, including Type V cement. But as for the brucite layer, it must be pointed out that the thickness of the aragonite deposit varies greatly from one prism to another one, from one side of a prism to another and even from place to place on the same side.

The internal microstructure of mortars as observed by SEM is very complex, and moreover it has to be recalled that SEM examinations are made

on fracture surfaces of the samples, and the fracture path is never random. It follows the weakest path. Consequently, no conclusion at all on the average amounts of the various phases present in the mortars can be drawn from SEM fracture examination, even on a semi-quantitative basis. But, on the other hand, since the fracture path follows the weakest zones, some information may be obtained on the relative weakening effect of various phases in the structure.

With regard to CSH, as is usual in mature cement pastes, most of the CSH present in all mortars studied is Type III (as per Diamond classification (27)) i.e. a very compact CSH with a rather nondescript character consisting of very small, irregularly equant or flattened particles. Type II ("reticular network") is observed too, both in water-cured mortars and mortars exposed to seawater. This Type II CSH morphology seems different after seawater exposure but the effect is not generally as evident as it could appear to be from Fig. 10, since many intermediate morphologies are observed. Consequently, more investigations should be carried out to ascertain if the CSH morphology is actually modified. Moreover, it must be pointed out that this "modification" of CSH occurs in all mortars, regardless of their strength losses.

Some EDX microanalysis performed on mortar polished sections shows the presence of Cl and SO_3 in CSH after exposure to seawater, but only about 1 % Cl and 1 % SO_3 which is much less Cl than found by Regourd (16).

Ettringite is rather easily detected in cements A and F mortars exposed to seawater. Most of it has a different morphology from the usual one, found in water-cured samples (this "normal" ettringite morphology consists of scattered small (approximately 0.5 μm diameter and approximately 4 μm long) hexagonal rods protruding through the CSH). It is observed either as "balls" of rather thick (approximately 1 μm diameter) and long (approximately 10 μm) hexagonal rods (Fig. 11) or as jumbles of very long needles (upper section of Fig. 11 a). Moreover this ettringite is not stoichiometric $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 32 \text{H}_2\text{O}$. It contains up to about 5 % SiO_2 and a small quantity of Cl (approximately 0.2 % Cl). As checked by XRD, this Si-ettringite is not the thaumasite observed in a 130 - years old concrete exposed to seawater (29). But since EDX microanalysis cannot detect carbon, it is impossible to say whether it is woodfordite $(\text{Ca}_6 \text{Al}_{1,5} (\text{SO}_4 \cdot \text{SiO}_3 \cdot \text{CO}_3) (\text{OH})_{10,5} \cdot 15 \text{H}_2\text{O})$ as found in a sulphate damaged tunnel (30) or simply ettringite in which some Al_2O_3 , and perhaps SO_3 , is replaced by SiO_2 as prepared by Lukas (31).

Some, but very little, Si - ettringite in "balls" could also be observed in cement C mortars after exposure to seawater. By contrast, only the usual (water-cured type one) ettringite was detected in cements B and D mortars.

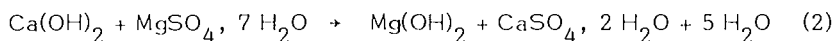
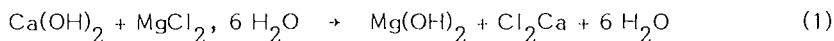
Calcium chloroaluminate is very difficult to distinguish in all the mortars. When observed, it was found mostly in druses where it occurs as well developed hexagonal plates. Moreover some was also detected, as checked by EDX microanalysis, as a rather indistinct plate-like formation in cements C and D mortars (Fig. 12 a). Finally, but only in one case, some

calcium chloroaluminate was observed next to a Si – ettringite ball in cement A mortar (Fig. 12 b). According to the EDX microanalysis, it contains small quantities of SiO_2 and SO_3 .

Calcium chlorosilicate was detected in C_3S mortars exposed to seawater, but only on polished section. Its average composition is $(\text{CaO})_{3.4} (\text{SiO}_2)_{3.6} (\text{CaCl}_2)_{0.6} \cdot n \text{H}_2\text{O}$ with approximately 1 % SO_3 . A few gypsum crystals have also been observed in these C_3S mortars, but not in any industrial cements mortars.

DISCUSSION

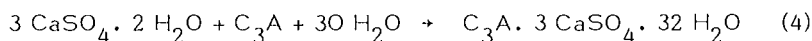
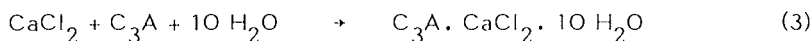
All our results lead to the conclusion that, at least under our experimental conditions, when a mortar is exposed to seawater, after a short period while there is ion exchange, the mortar becomes almost completely isolated from the seawater. One possible explanation of this phenomenon is the formation of a protective layer around the mortar as previously postulated (18, 21, 27) but never proven. In fact, two layers are observed. First a $\text{Mg}(\text{OH})_2$ (brucite) layer is formed. The reactions which occur are :



By contrast, according to our observations (long-term stability of brucite, thinner brucite layer formed on type V cement mortar, no appearance of magnesium silicate hydrate) no reaction between CSH and $\text{MgCl}_2, 6 \text{H}_2\text{O}$ and $\text{MgSO}_4, 7 \text{H}_2\text{O}$ is likely to occur.

Simultaneously with brucite formation, calcite deposits present on the mortars dissolves away and aragonite is formed. After about 3 months, this aragonite has become a continuous layer. So, at this stage, both brucite and aragonite layers are very dense and are undoubtedly able to protect the mortar from further ion penetration. But it is not possible to know whether both, or only one layer, is needed. Brucite has already precipitated after two days exposure to seawater and there is still Cl and SO_3 diffusion. But brucite crystallisation is not advanced at this stage and the layer may still be permeable. On the other hand, the aragonite does not form a continuous deposit after only 1 month exposure, yet SO_3 diffusion is already arrested.

Regarding seawater attack, and may be because of this protection phenomenon, influence of C_3A content is not at all obvious. When CaCl_2 and $\text{CaSO}_4, 2 \text{H}_2\text{O}$ formed by reactions (1) and (2) diffuse into the mortar, most of it reacts with C_3A :



The amounts of calcium chloroaluminate and ettringite formed can be calculated from the average Cl and SO_3 present in the mortars, together

with the resulting increases in volume. Then, if these results are compared to the XRD data and the strength losses the following comments can be made :

1. There is good agreement between the amounts of calcium chloroaluminate and ettringite obtained by XRD and chemical analysis, except for cement D mortars (at all ages) and for cement F mortars after more than 1 year exposure. In the first case, the explanation, as previously given, is poor crystallisation of Fe – ettringite. The second case is much more complex and might be correlated with a partial decomposition of stoichiometric ettringite and Si – ettringite formation occurring with Ca(OH)_2 consumption.
2. Considering increases in volume during reactions (3) and (4), and strength losses, it may be concluded that calcium chloroaluminate plays a more important part in seawater attack than ettringite. But this conclusion is negated by the SEM examinations. We prefer to conclude, in agreement with Heller (9), that increase of volume accompanying calcium chloroaluminate crystallisation can be accommodated by the pores and consequently does not lead to strength losses (it could even increase the strength by lowering the porosity of the cement paste).
3. Despite their relatively high contents of calcium chloroaluminate and ettringite, cement C mortars show very small strength losses. But no "balls" of Si – ettringite could be detected by SEM whilst they were readily evident in cements A and F mortars which have deteriorated most. In view of this, it can be concluded that a consequential effect of seawater attack would not be the total amount of ettringite present in the mortar but the formation of Si – ettringite. Nevertheless, it does not explain why this reaction which occurs in cement A and F mortars, does not occur in cement C mortars. All three cements have a similar composition and the same C_3A content (as appears from Bogue calculation and was checked by the selective dissolutions technique). Moreover it cannot be attributed to the crystallographic form of C_3A , since C_3A in cement C is cubic as in cement A, whilst it is orthorhombic in cement F.

CONCLUSION

The results obtained in this study show that the formation of a protective layer (Mg(OH)_2 and/or aragonite) plays an important part in the mechanism of seawater attack on cement mortar. No significant influence of C_3A content could be detected (for instance one of the three cements investigated which contain 13 % C_3A gives a mortar as durable as a zero – C_3A cement). This is confirmed by much more numerous compressive strength loss tests performed on all types of cements in our Central Laboratory. That this indistinct influence of C_3A should be attributed only to the protective layer effect seems probable. Another well-known factor is the porosity of the mortar, and the studied mortars were rather compact. Consequently, supplementary experiments with more porous mortars are planned. Besides, the influence of alternative immersion and drying over 8 – hours periods will be studied since the protective layer may be damaged under the field conditions, especially at tide level. Such studies should help to

improve our knowledge of chemical factors, for instance, the very important question of the conditions of formation and the weakening effect of the Si - ettringite which was observed in this investigation.

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TABLE 1 - Chemical Composition of Artificial Sea-water Used

Na Cl	:	32 g/l
Mg Cl ₂ , 6 H ₂ O	:	6 g/l
Mg SO ₄ , 7 H ₂ O	:	5 g/l
Ca SO ₄ , 2 H ₂ O	:	1,5 g/l
K H CO ₃	:	0,2 g/l

TABLE 2 - Chemical and Mineralogical Composition of Cements Investigated

	A (Type I)	B (Type I)	C (Type I)	D (Type V)	E (C ₃ S)	F (Type I)
SiO ₂	20.45	22.90	20.25	24.45	25.95	19.45
Al ₂ O ₃	6.65	2.95	6.45	2.55	0.80	6.80
Fe ₂ O ₃	2.50	0.25	2.10	4.50	0.10	2.60
CaO	63.10	69.60	63.15	62.95	72.45	63.10
MgO	1.65	0.50	2.35	1.20	0	1.00
SO ₃	3.10	1.70	3.10	1.90	0	2.80
K ₂ O	1.25	0.23	1.12	0.24	0	1.34
Na ₂ O	0.13	0.14	0.12	0.07	0	0.22
Insoluble residue	0.60	0.10	0.20	0.10	0	0.15
Ignition loss	1.35	2.05	0.75	1.45	0.10	2.10
Free CaO	1.30	6.35	0.40	0.55	0.45	1.95
C ₃ S *	48.4	57.6	57.5	40.8	90.3	45.3
C ₂ S	20.5	22.0	14.2	39.1	6.8	21.2
C ₃ A	13.4	7.4	13.55	0	2.0	13.6
C ₄ AF	7.6	0.8	6.40	13.7	0.3	7.9
Cristallographic form of C ₃ A	cubic	cubic	cubic	-	-	orthorhombic

* computed by Bogue formula.